

FORM PTO-1390
(REV. 11-2000)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

268/200

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

10/031108

INTERNATIONAL APPLICATION NO.

PCT/EP00/06422

INTERNATIONAL FILING DATE

July 6, 2000

PRIORITY DATE CLAIMED

July 13, 1999

TITLE OF INVENTION

NANOCOMPOSITES

APPLICANT(S) FOR DO/EO/US

Carsten ZILG; Rolf MÜLHAUPT; Jürgen FINTER

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ is attached hereto (required only if not communicated by the International Bureau)
 - b. ☒ has been communicated by the International Bureau
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4)
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☐ A **FIRST** preliminary amendment.
14. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 – 1.825.
18. ☒ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information: **PCT/IB/308**

U.S. APPLICATION NO. (if known, see 37 CFR 1.5)

10/031108

INTERNATIONAL APPLICATION NO.

PCT/EP00/06422

ATTORNEY'S DOCKET NUMBER

268/20021. ☒ The following fees are submitted:**BASIC NATIONAL FEE (37 CFR 1.492(a)(1) – (5)):**

Neither international preliminary examination fee (37 CFR 1.482)
nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO
and International Search Report not prepared by the EPO or JPO **\$1040.00**

International preliminary examination fee (37 CFR 1.482) not paid to
USPTO but International Search Report prepared by the EPO or JPO **\$890.00**

International preliminary examination fee (37 CFR 1.482) not paid to USPTO
but international search fee (37 CFR 1.445(a)(2)) paid to USPTO **\$740.00**

International preliminary examination fee (37 CFR 1.482) paid to USPTO
but all claims did not satisfy provisions of PCT Article 33(1)-(4) **\$710.00**

International preliminary examination fee (37 CFR 1.482) paid to USPTO
and all claims satisfied provisions of PCT Article 33(1)-(4) **\$100.00**

ENTER APPROPRIATE BASIC FEE AMOUNT =**CALCULATIONS PTO USE ONLY****\$890.00**

Surcharge of **\$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30
months from the earliest claimed priority date (37 CFR 1.492(e)).

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$
Total claims	14 - 20 =	0	x \$18.00	\$
Independent claims	3 - 3 =	0	x \$80.00	\$
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$270.00	\$
TOTAL OF ABOVE CALCULATIONS =				\$890.00
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				\$
SUBTOTAL =				\$890.00
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$
TOTAL NATIONAL FEE =				\$890.00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property				\$40.00
TOTAL FEES ENCLOSED =				\$930.00
				Amount to be refunded: \$
				charged: \$

a. ☐ A check in the amount of \$ to cover the above fees is enclosed.

b. ☒ Please charge my Deposit Account No. 12-2475 in the amount of \$930.00 to cover the above fees. A duplicate copy of this
sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to
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d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information
should not be included on this form.** Provide credit card information and authorization on PTO-2038.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a)
or (b)) must be filed and granted to restore the application to pending status.

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REGISTRATION NUMBER

10/031108

JCS REG. NO. 10 JAN 2002

CERTIFICATE OF MAILING
(37 C.F.R. §1.10)

I hereby certify that this paper (along with any referred to as being attached or enclosed) is being deposited with the United States Postal Service on the date shown below with sufficient postage as 'Express Mail Post Office To Addressee' in an envelope addressed to Box PCT, Commissioner for Patents, Washington, D.C. 20231.

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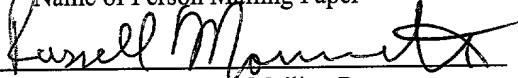
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2002-01-10

Nanocomposites

The present invention relates to compositions composed of specific resin mixtures and organophilic layer silicates, to a process for the preparation of nanocomposites and to their use.

The preparation of organophilic layer silicates by treatment of layer silicates with onium salts, e.g. quaternary ammonium salts, in the presence of a dispersion medium is known from US Patent No. 4 810 734. In that treatment an exchange of ions takes place, the cation of the onium salt being inserted into the interlayer space of the layer silicate. Layer silicates modified in that manner become organophilic as a result of the organic radical of the intercalated amine. When that organic radical contains functional groups, the organophilic layer silicate is capable of forming chemical bonds with suitable monomers or polymers.

WO 96/08526 describes the use of such organophilic layer silicates as filler materials for epoxy resins, there being obtained nanocomposites having improved physical and mechanical properties. It is of special interest that there is an increase in rigidity while the toughness at least remains the same. Especially good properties are exhibited by nanocomposites that contain the layer silicate in exfoliated form.

However, the addition of such organophilic layer silicates gives rise not only to an improvement in rigidity but also to a reduction in tensile strength.

It has now been found, surprisingly, that a combination of organophilic layer silicates and epoxidised or maleinated synthetic or natural oils results in nanocomposites having considerably improved mechanical properties. For example, in the preparation of the nanocomposites according to the invention not only are the rigidity and toughness considerably increased in comparison with the unmodified material, but the tensile strength is maintained at the level of the unmodified material. In addition, it is possible to incorporate large proportions of epoxidised or maleinated synthetic or natural oils into the nanocomposites according to the invention and thus to achieve a considerable reduction in total cost without there being any appreciable impairment of the mechanical properties of the nanocomposites according to the invention. By varying the ratio of epoxidised or maleinated oil to organophilic three-layer silicate it is possible to obtain tailored system-specific property profiles.

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The present invention relates to a composition comprising

(A) a resin mixture consisting of

(A1) from 0.5 to 50.0 % by weight, based on the sum of components A1 + A2, of an epoxidised or maleinated natural or synthetic oil, and

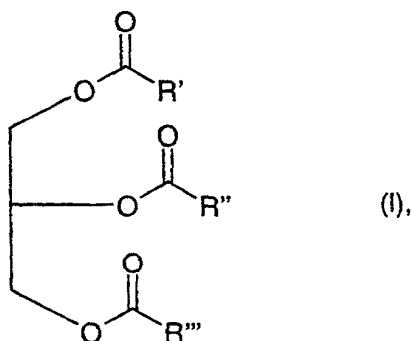
(A2) from 50.0 to 99.5 % by weight, based on the sum of components A1 + A2, of a polymerisable or curable monomer or monomer mixture other than A1, and

(B) an organophilic layer silicate obtainable by treatment of a natural or synthetic layer silicate with a swelling agent selected from sulfonium, phosphonium and ammonium compounds, but in the case where component A1 is an epoxidised oil, salts of melamine compounds and cyclic amidine compounds are excluded as ammonium compounds.

As component A1 there may be used the epoxidation products of natural or synthetic oils and the reaction products of natural or synthetic oils with maleic acid anhydride.

Suitable natural oils are, for example, unsaturated fatty acid esters. It is preferable to use compounds that are derived from mono- and poly-fatty acids having from 12 to 22 carbon atoms and an iodine number of from 30 to 400, for example lauroleic acid, myristoleic acid, palmitoleic acid, oleic acid, gadoleic acid, erucic acid, ricinoleic acid, linoleic acid, linolenic acid, elaidic acid, licanic acid, arachidonic acid and clupanodonic acid.

Preferred components A1 are derived from triglycerides of formula I



wherein R', R'' and R''' are each independently of the others saturated or unsaturated fatty acid radicals having from 12 to 25 carbon atoms, but at least one of the radicals R', R'' and R''' is an unsaturated fatty acid radical.

Examples of natural oils are soybean oil, linseed oil, perilla oil, tung oil, oiticica oil, safflower

oil, poppyseed oil, hemp oil, cottonseed oil, sunflower oil, rapeseed oil, walnut oil, beet oil, high oleic triglycerides, triglycerides from euphorbia plants, groundnut oil, olive oil, olive kernel oil, almond oil, kapok oil, hazelnut oil, apricot kernel oil, beechnut oil, lupin oil, maize oil, sesame oil, grapeseed oil, lallemantia oil, castor oil, herring oil, sardine oil, menhaden oil, whale oil, tall oil, palm oil, palm kernel oil, coconut oil, cashew oil and tallow oil and derivatives derived therefrom.

Also suitable are higher unsaturated derivatives that can be obtained by subsequent dehydration reactions of those oils.

Examples of synthetic oils suitable for the preparation of component A1 are polybutadiene oils, polyethylene oils, polypropylene oils, polypropylene oxide oils, polyethylene oxide oils and paraffin oils.

As component A1 for the preparation of the compositions according to the invention it is also possible to use adducts of epoxy resins with fatty acids and also adducts of epoxy resins with the above-mentioned epoxidised or maleinated oils.

It is preferable to use as component A1 an epoxidised or maleinated oil based on mono- and poly-fatty acids having from 12 to 22 carbon atoms or an epoxidised or maleinated rubber.

Especially preferred components A1 are epoxidised or maleinated soybean oil and linseed oil.

Suitable as component A2 are monomers or monomer mixtures that can be polymerised to form solid thermoplastics or polycondensed or polyadded to form crosslinked thermosets, either by irradiation or heating, optionally in the presence of initiators.

Preferred components A2 are the monomers or oligomers that can be used for the preparation of thermosetting polymer systems.

Thermosetting polymer systems can be used in the form of polycondensates or polyadducts. Thermosetting plastics in the form of polycondensates are, for example, curable phenol/formaldehyde plastics (PF casting resins), curable bisphenol resins, curable urea/formaldehyde plastics (UF moulding materials), polyimides (PI), bismaleinimide moulding materials (BMI) and

polybenzimidazoles (PBI). Thermosetting plastics in the form of polyadducts are, for example, epoxy resins (EP), moulding materials of unsaturated polyester resins (UP moulding materials), DAP resins (polydiallyl phthalate), melamine/formaldehyde resins, e.g. curable melamine/-phenol/formaldehyde moulding materials, and crosslinked polyurethanes (PUR).

Preference is given to polyurethane and epoxy resin systems, that is to say in the compositions according to the invention the component A2 is preferably a mixture of a polyisocyanate and a polyol or a mixture of an epoxy resin having more than one 1,2-epoxy group in the molecule and a hardener for the epoxy resin.

Examples of suitable epoxy resins are:

I) Polyglycidyl and poly(β -methylglycidyl) esters, obtainable by reaction of a compound having at least two carboxyl groups in the molecule with epichlorohydrin and β -methyl-epichlorohydrin, respectively. The reaction is advantageously carried out in the presence of bases. Aliphatic polycarboxylic acids can be used as the compound having at least two carboxyl groups in the molecule. Examples of such polycarboxylic acids are oxalic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, sebacic acid, suberic acid, azelaic acid and dimerised or trimerised linoleic acid. It is also possible, however, to use cycloaliphatic polycarboxylic acids, for example tetrahydrophthalic acid, 4-methyltetrahydrophthalic acid, hexahydrophthalic acid or 4-methylhexahydrophthalic acid. Aromatic polycarboxylic acids, for example phthalic acid, isophthalic acid or terephthalic acid, may also be used.

II) Polyglycidyl or poly(β -methylglycidyl) ethers, obtainable by reaction of a compound having at least two free alcoholic hydroxy groups and/or phenolic hydroxy groups with epichlorohydrin or β -methylepichlorohydrin under alkaline conditions, or in the presence of an acidic catalyst and subsequent alkali treatment. The glycidyl ethers of this kind may be derived, for example, from acyclic alcohols, such as from ethylene glycol, diethylene glycol and higher poly(oxyethylene) glycols, propane-1,2-diol or poly(oxypropylene) glycols, propane-1,3-diol, butane-1,4-diol, poly(oxytetramethylene) glycols, pentane-1,5-diol, hexane-1,6-diol, hexane-2,4,6-triol, glycerol, 1,1,1-trimethylolpropane, pentaerythritol, sorbitol and also from polyepichlorohydrins, but they may also be derived, for example, from cycloaliphatic alcohols, such as 1,4-cyclohexanedimethanol, bis(4-hydroxycyclohexyl)methane or 2,2-bis(4-hydroxycyclohexyl)propane, or they may have aromatic nuclei, such as N,N-bis(2-hydroxyethyl)-

aniline or p,p'-bis(2-hydroxyethylamino)diphenylmethane. The glycidyl ethers may also be derived from mononuclear phenols, for example from resorcinol or hydroquinone, or they may be based on polynuclear phenols, for example bis(4-hydroxyphenyl)methane, 4,4'-dihydroxybiphenyl, bis(4-hydroxyphenyl)sulfone, 1,1,2,2-tetrakis(4-hydroxyphenyl)ethane, 2,2-bis(4-hydroxyphenyl)propane, 2,2-bis(3,5-dibromo-4-hydroxyphenyl)propane and also on novolaks, obtainable by condensation of aldehydes, such as formaldehyde, acetaldehyde, chloral or furfuraldehyde, with phenols, such as phenol, or with phenols substituted in the nucleus by chlorine atoms or C₁-C₉alkyl groups, for example 4-chlorophenol, 2-methylphenol or 4-tert-butylphenol, or by condensation with bisphenols, such as those of the kind mentioned above.

III) Poly(N-glycidyl) compounds, obtainable by dehydrochlorination of the reaction products of epichlorohydrin with amines that contain at least two amine hydrogen atoms. Such amines are, for example, aniline, n-butylamine, bis(4-aminophenyl)methane, m-xylylenediamine and bis(4-methylaminophenyl)methane. Poly(N-glycidyl) compounds also include, however, triglycidyl isocyanurate, N,N'-diglycidyl derivatives of cycloalkyleneureas, such as ethyleneurea or 1,3-propyleneurea, and diglycidyl derivatives of hydantoins, such as of 5,5-dimethylhydantoin.

IV) Poly(S-glycidyl) compounds, for example di-S-glycidyl derivatives, derived from dithiols, for example ethane-1,2-dithiol or bis(4-mercaptomethylphenyl) ether.

V) Cycloaliphatic epoxy resins, for example bis(2,3-epoxycyclopentyl) ether, 2,3-epoxycyclopentylglycidyl ether, 1,2-bis(2,3-epoxycyclopentyl)ethane or 3,4-epoxycyclohexylmethyl 3',4'-epoxycyclohexanecarboxylate.

It is also possible, however, to use epoxy resins in which the 1,2-epoxy groups are bonded to different hetero atoms or functional groups; these compounds include, for example, the N,N,O-triglycidyl derivative of 4-aminophenol, the glycidyl ether glycidyl ester of salicylic acid, N-glycidyl-N'-(2-glycidylloxypropyl)-5,5-dimethylhydantoin or 2-glycidylloxy-1,3-bis(5,5-dimethyl-1-glycidylhydantoin-3-yl)propane.

It is preferable to use as epoxy resin in the curable mixtures according to the invention a fluid or viscous polyglycidyl ether or ester, especially a fluid or viscous bisphenol diglycidyl ether.

Bisphenol A diglycidyl ether and bisphenol F diglycidyl ether are especially preferred.

The above-mentioned epoxy compounds are known and some of them are commercially available. It is also possible to use mixtures of epoxy resins.

All customary hardeners for epoxides can be used; preferred hardeners are amines, carboxylic acids, carboxylic acid anhydrides and phenols. It is also possible to use catalytic hardeners, for example imidazoles. Such hardeners are described, for example, in H. Lee, K. Neville, Handbook of Epoxy Resins, McGraw Hill Book Company, 1982. The amount of hardening agent used is governed by the chemical nature of the hardening agent and by the desired properties of the curable mixture and of the cured product. The maximum amount can readily be determined by a person skilled in the art. The preparation of the mixtures can be carried out in customary manner by mixing the components together by manual stirring or with the aid of known mixing apparatus, for example by means of stirrers, kneaders or rollers. Depending upon the application, conventionally used additives, for example fillers, pigments, colourings, flow agents or plasticisers, may be added to the mixtures.

Further preferred components A2 are polyurethane precursors. Structural components for crosslinked polyurethanes are polyisocyanates, polyols and optionally polyamines, in each case having two or more of the respective functional groups per molecule.

Aromatic and also aliphatic and cycloaliphatic polyisocyanates are suitable building blocks for polyurethane chemistry. Examples of frequently used polyisocyanates are 2,4- and 2,6-diisocyanatotoluene (TDI) and mixtures thereof, especially the mixture of 80 % by weight 2,4-isomer and 20 % by weight 2,6-isomer; 4,4'- and 2,4'- and 2,2'-methylenediisocyanate (MDI) and mixtures thereof and technical grades that, in addition to containing the above-mentioned simple forms having two aromatic nuclei, may also contain polynuclear forms (polymer MDI); naphthalene-1,5-diisocyanate (NDI); 4,4',4''-triisocyanatotriphenylmethane and 1,1-bis(3,5-diisocyanato-2-methyl)-1-phenylmethane; 1,6-hexamethylene diisocyanate (HDI) and 1-isocyanato-3-(isocyanatomethyl)-3,5,5-trimethylcyclohexane (isophorone diisocyanate, IDPI). Such basic types of polyisocyanates may optionally also have been modified by dimerisation or trimerisation with the formation of corresponding carbodiimides, uretdiones, biurets or allophanates.

Especially preferred polyisocyanates are the various methylene diisocyanates, hexamethylene diisocyanate and isophorone diisocyanate.

As polyols there may be used in the polyurethane production both low molecular weight compounds and oligomeric and polymeric polyhydroxyl compounds. Suitable low molecular weight polyols are, for example, glycols, glycerol, butanediol, trimethylolpropane, erythritol, pentaerythritol; pentitols, such as arabitol, adonitol or xylitol; hexitols, such as sorbitol, mannitol or dulcitol, various sugars, for example saccharose, or sugar and starch derivatives. Low molecular weight reaction products of polyhydroxyl compounds, such as those mentioned, with ethylene oxide and/or propylene oxide are also frequently used as polyurethane components, as well as the low molecular weight reaction products of other compounds that contain sufficient numbers of groups capable of reaction with ethylene oxide and/or propylene oxide, for example the corresponding reaction products of amines, such as especially ammonia, ethylenediamine, 1,4-diaminobenzene, 2,4-diaminotoluene, 2,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, 1-methyl-3,5-diethyl-2,4-diaminobenzene and/or 1-methyl-3,5-diethyl-2,6-diaminobenzene. Further suitable polyamines are given in EP-A-0 265 781.

As long-chain polyol components there are used chiefly polyester polyols, including polylactones, for example polycaprolactones, and polyether polyols.

The polyester polyols are generally linear hydroxyl polyesters having molar masses of approximately from 1000 to 3000, preferably up to 2000.

Suitable polyether polyols preferably have a molecular weight of about from 300 to 8000 and can be obtained, for example, by reaction of a starter with alkylene oxides, for example with ethylene, propylene or butylene oxides or tetrahydrofuran (polyalkylene glycols). Starters that come into consideration are, for example, water, aliphatic, cycloaliphatic or aromatic polyhydroxyl compounds having generally 2, 3 or 4 hydroxyl groups, such as ethylene glycol, propylene glycol, butanediols, hexanediols, octanediols, dihydroxybenzenes or bisphenols, e.g. bisphenol A, trimethylolpropane or glycerol, or amines (see Ullmanns Encyclopädie der technischen Chemie, 4th edition, Vol. 19, Verlag Chemie GmbH, Weinheim 1980, pages 31-38 and pages 304, 305). Especially preferred kinds of polyalkylene glycols are polyether

polyols based on ethylene oxide and polyether polyols based on propylene oxide, and also corresponding ethylene oxide/propylene oxide copolymers, it being possible for such polymers to be statistical or block copolymers. The ratio of ethylene oxide to propylene oxide in such copolymers may vary within wide limits. For example, only the terminal hydroxyl groups of the polyether polyols may have been reacted with ethylene oxide (end capping). The content of ethylene oxide units in the polyether polyols may also, however, have values of e.g. up to 75 or 80 % by weight. It will frequently be advantageous for the polyether polyols to be at least end-capped with ethylene oxide, since in that case they will have terminal primary hydroxyl groups which are more reactive than the secondary hydroxyl groups originating from the reaction with propylene oxide. Special mention should also be made of polytetrahydrofurans which, like the polyalkylene glycols already mentioned above, are commercially available (trade name e.g. POLYMEG®). The preparation and properties of such polytetrahydrofurans are described in greater detail, for example, in Ullmanns Encyclopädie der technischen Chemie, 4th edition, Vol. 19, Verlag Chemie GmbH, Weinheim 1980, pages 297 - 299.

Also suitable as components of polyurethanes are polyether polyols that contain solid organic fillers in disperse distribution and chemically partially bonded to the polyether, such as polymer polyols and polyurea polyols. Polymer polyols are, as is known, polymer dispersions that can be prepared by free-radical polymerisation of suitable olefinic monomers, especially acrylonitrile or styrene or mixtures of the two, in a polyether serving as graft base. Polyurea polyols (PHD polyethers), which can be prepared by reaction of polyisocyanates with polyamines in the presence of polyether polyols, are dispersions of polyureas in polyether polyols, there likewise taking place a partially chemical linkage of the polyurea material to the polyether polyols by way of the hydroxyl groups on the polyether chains. Polyols such as those mentioned in this section are described in greater detail, for example, in Becker/Braun "Kunststoffhandbuch", Vol. 7 (Polyurethanes), 2nd edition, Carl Hanser Verlag, Munich, Vienna (1983), pages 76, 77.

Polyamines also play an important role as components in the preparation of polyurethanes, especially because they exhibit greater reactivity than comparable polyols. As in the case of the polyols, both low molecular weight polyamines, e.g. aliphatic or aromatic di- and polyamines, and polymeric polyamines, e.g. poly(oxyalkylene)polyamines, can be used.

Suitable poly(oxyalkylene)polyamines, which, for example, in accordance with US Patent 3 267 050 are obtainable from polyether polyols, preferably have a molecular weight of from 1000 to 4000 and are also commercially available, e.g. under the name JEFFAMINE[®], such as JEFFAMINE[®]D 2000, an amino-terminated polypropylene glycol of the general formula $H_2NCH(CH_3)CH_2-[OCH_2CH(CH_3)]_x-NH_2$, wherein x has on average the value 33, resulting in a total molecular weight of about 2000; JEFFAMINE[®]D 2001 having the formula $H_2NCH(CH_3)CH_2-[OCH_2CH(CH_3)]_a-[OCH_2CH_2]_b-[OCH_2CH(CH_3)]_c-NH_2$, wherein b is on average about 40.5 and a+c is about 2.5; JEFFAMINE[®]BUD 2000, a urea-terminated polypropylene ether of formula $H_2N(CO)NH-CH(CH_3)CH_2-[OCH_2CH(CH_3)]_n-NH(CO)NH_2$, wherein n is on average about 33, resulting in a molecular weight of about 2075; or JEFFAMINE[®]T 3000, a glycerol-started poly(oxypropylene)triamine having a molecular weight of about 3000.

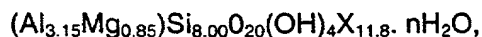
For the preparation of polyurethanes there are often used mixtures of one or more polyols and/or one or more polyamines, as described, for example, in EP-A-0 512 947, EP-A-0 581 739 or the prior art cited in those documents.

As layer silicates for the preparation of the organophilic layer silicates according to component B of the compositions of the invention there come into consideration especially natural and synthetic smectite clay minerals, more especially bentonite, vermiculite, halloysite, saponite, beidellite, nontronite, hectorite, sauconite, stevensite and montmorillonite.

Montmorillonite and hectorite are preferred.

The layer silicate montmorillonite, for example, corresponds generally to the formula $Al_2[(OH)_2/Si_4O_{10}] \cdot nH_2O$, it being possible for some of the aluminium to have been replaced by magnesium. The composition varies according to the silicate deposit.

A preferred composition of the layer silicate corresponds to the formula



wherein X is an exchangeable cation, generally sodium or potassium, and some of the hydroxyl groups may have been replaced by fluoride ions.

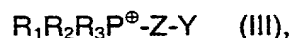
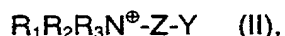
By exchanging hydroxyl groups for fluoride ions, synthetic layer silicates are obtained.

Special preference is given to layer silicates in which the layers have a layer spacing of about from 0.7 nm to 1.2 nm and which have a cation exchange capacity in the region of 50 to 200 meq./100 g (milliequivalents per 100 grams). After treatment with the swelling agent (sulfonium, phosphonium or ammonium compound), the layer spacing in the organophilic layer silicates so obtained is preferably at least 1.2 nm.

Such layer silicates are described, for example, in A.D. Wilson, H.T. Posser, Developments in Ionic Polymers, London, Applied Science Publishers, Chapter 2, 1986. Synthetic layer silicates can be obtained, for example, by reaction of natural layer silicates with sodium hexafluorosilicate and are commercially available *inter alia* from the CO-OP Chemical Company, Ltd., Tokyo, Japan.

The sulfonium, phosphonium and ammonium compounds required as swelling agents for the preparation of the organophilic layer silicates according to component B of the compositions of the invention are known and some of them are commercially available. They are generally compounds having an onium ion, for example trimethylammonium, trimethylphosphonium and dimethylsulfonium, and a functional group that is capable of reacting or bonding with a polymeric compound. Suitable ammonium salts can be prepared, for example, by protonation or quaternisation of corresponding aliphatic, cycloaliphatic or aromatic amines, diamines, polyamines or aminated polyethylene or polypropylene glycols (Jeffamine® M series, D series or T series).

Suitable swelling agents are, for example, salts that contain cations of formulae II-IV



wherein R_1 , R_2 and R_3 are each independently of the others hydrogen or C_1 - C_6 alkyl, Z is the divalent radical of a C_2 - C_{30} alkane that is unsubstituted or substituted by one or more phenyl groups, C_1 - C_4 alkoxy groups, hydroxyl groups or halogen atoms and Y is -OH, -COOH, -NH₂, vinyl, glycidyl or β -methylglycidyl.

It is preferable to use as swelling agents ammonium salts that are obtainable by reaction of amino acids with mineral acids.

Especially preferred are salts of 4-aminobutyric acid, 6-aminocaproic acid, ω -aminocaprylic acid, 10-aminodecanoic acid, 12-aminododecanoic acid, 14-aminotetradecanoic acid, 16-aminohexadecanoic acid and 18-aminooctadecanoic acid.

For the preparation of the organophilic layer silicates according to component B of the compositions of the invention, the swelling agent is first advantageously dispersed or dissolved, with stirring, in a dispersion medium, preferably at elevated temperature of about from 40°C to 90°C. The layer silicate is then added and dispersed, with stirring. The organophilic layer silicate so obtained is filtered off, washed with water and dried.

It is, of course, also possible to prepare the dispersion of the layer silicate as initial batch and then to add the solution or dispersion of the swelling agent.

Suitable dispersion media are water, methanol, ethanol, propanol, isopropanol, ethylene glycol, 1,4-butanediol, glycerol, dimethyl sulfoxide, N,N-dimethylformamide, acetic acid, formic acid, pyridine, aniline, phenol, nitrobenzene, acetonitrile, acetone, 2-butanone, chloroform, carbon disulfide, propylene carbonate, 2-methoxyethanol, diethyl ether, tetrachloromethane and n-hexane. Preferred dispersion media are methanol, ethanol and especially water.

The swelling agent brings about a widening of the interlayer spacing of the layer silicate, so that the layer silicate is able to take up monomers into the interlayer space. The subsequent polymerisation, polyaddition or polycondensation of the monomer or monomer mixture results in the formation of a composite material, a nanocomposite.

Various process variants can be employed for the preparation of the nanocomposites according to the invention:

the swelling agent can be inserted into the layer silicate by cation exchange and the resulting organophilic layer silicate can then be incorporated as filler into the resin mass or into one of the components of the resin mass.

It is also possible, however, firstly to adduct the swelling agent with the epoxidised or maleinated oil or with a portion of the monomer or monomer mixture, insert the resulting product into the layer silicate and then process that mass with the remaining portion of the resin mixture to form a moulding material.

The quantity ratio of components A and B in the compositions according to the invention may vary within wide limits. The proportion of component B is preferably from 0.5 to 30 % by weight, especially from 2 to 20 % by weight and more especially from 5 to 15 % by weight, based on the weight of component A.

In addition to components A and B, the compositions according to the invention may contain further customary additives, for example catalysts, stabilisers, propellants, parting agents, fireproofing agents, fillers and pigments, *etc.*

The invention relates also to a process for the preparation of a nanocomposite, wherein a composition comprising components A and B is solidified by curing or polymerisation of component A.

Special preference is given to nanocomposites that contain the layer silicate in exfoliated form.

By virtue of the very good property profile of the nanocomposites, the compositions according to the invention have a wide variety of uses, *inter alia* as coatings, paints/varnishes or adhesives.

The nanocomposites according to the invention can be processed by customary methods of plastics processing, such as injection moulding or extrusion, or other methods of shaping to form finished mouldings. Epoxy resins can be used as casting resins.

The present invention relates also to the use of the compositions according to the invention in the production of paints/varnishes, adhesives, casting resins, coatings, fireproofing agents, thixotropic agents or reinforcing agents.

The following Examples illustrate the invention.

Example 1: Synthesis of 12-aminododecanoic acid hydrochloride and the three-layer silicate organophilically modified therewith

96.96 g of 12-aminododecanoic acid are heated in 4 litres of deionised water in a glass beaker and, with stirring, 48 ml of concentrated hydrochloric acid are added. 200 g of the

synthetic three-layer silicate Somasif ME 100 from CO-OP-Chemicals, Japan, are then added, with stirring, to the hot solution, a flocculent cream-coloured precipitate being formed. The precipitate is filtered off and washed with a total of 12 litres of hot deionised water, so that chloride can no longer be detected with 0.1N silver nitrate solution. The three-layer silicate so modified is dried at 80°C for 72 hours *in vacuo*. The product is referred to as Somasif ADS below.

The degree of charge is ascertained by thermogravimetric tests at 78 meq./100 g. Somasif ME 100 has a cation exchange capacity of 70-80 meq./100 g. Measurement of the layer spacing of the three-layer silicate by means of X-ray tests shows that it has increased from 0.94 nm to 1.6 nm.

Examples 2-6: Synthesis of the unmodified nanocomposites and the nanocomposites modified with epoxidised soybean oil (content of Somasif ADS 10 % by weight)

For the preparation of the nanocomposites, a mixture of epoxy resin 1 (99.71 parts by weight of bisphenol A diglycidyl ether having an epoxy number of 5.00-5.25 eq./kg + 0.29 parts by weight of tetramethylammonium chloride) and hardener 1 (Araldit® HY 925, methyltetrahydrophthalic acid anhydride) in a ratio by weight of 100 : 80 is selected. The mixture is modified with the organophilic layer silicate prepared in Example 1. The production of the mouldings is described by way of example below using the example of the 10 % by weight nanocomposite.

In a tin container, 300 g of epoxy resin 1 and 60 g of Somasif ADS are stirred in a planetary mixer for 1 hour at 80°C/13 mbar. 240 g of hardener 1 are then added. The reaction mixture is pregelled at 80°C/13 mbar, with stirring, to give a viscosity of about 20 000 mPa.s and then, for the production of mouldings, is introduced into steel moulds of dimensions 200×200×4 mm and fully cured at 140°C for 14 hours.

For the preparation of the modified nanocomposites, 1; 2.5; 5; 10; 20 % by weight of the epoxy component (epoxy resin 1) are replaced by epoxidised soybean oil (ESO). Again a ratio by weight of the epoxy component mixture (epoxy resin 1 + epoxidised soybean oil) to anhydride hardener (hardener 1) of 100 : 80 is selected. Each of the mixtures is then filled with Somasif ADS (10 % by weight). The preparation of such nanocomposites is described

by way of example below using the example of the moulding material modified with 50 % ESO.

In a tin container, 150 g of epoxy resin 1, 150 g of epoxidised soybean oil and 60 g of Somasif ADS are stirred for 1 hour at 80°C/13 mbar in a planetary mixer, and then 240 g of hardener 1 are added. The reaction mixture is pregelled at 80°C/13 mbar, with stirring, to give a viscosity of about 20 000 mPas and then, for the production of mouldings, is introduced into steel moulds of dimensions 200×200×4 mm and fully cured at 140°C for 14 hours. The cast mouldings are milled to give test specimens, which are subjected to a tension test in accordance with ISO 527/95 and a bend-notch test according to PM/258/90. The mechanical properties obtained therefrom are listed in Table 1 below.

Table 1:

Example	2	3	4	5	6
epoxy resin 1 [g]	297	292.5	285	270	240
ESO [g]	3	7.5	15	30	60
Somasif ADS [g]	60	60	60	60	60
hardener 1 [g]	240	240	240	240	240
modulus of elasticity [MPa]	4450	4420	4410	4360	4320
tensile strength [N/mm ²]	69	62	61	60	60
K _{1C} [MPa·m ^{1/2}]	1.04	1.05	0.98	1.04	1.01
G _{1C} [J/m ²]	223	231	199	225	214

It will be seen that by incorporating epoxidised soybean oil, a fall in the tensile strength of the nanocomposites can be prevented without there being a substantial fall in the elasticity moduli.

Examples 7-11: Synthesis of the nanocomposites modified with maleinated soybean oil (MASO) (content of Somasif ADS 10 % by weight)

For the preparation of these modified nanocomposites, 1; 2.5; 5; 10; 20 % by weight of the hardener component (hardener 1) are replaced by maleinated soybean oil (MASO). Again a ratio by weight of the epoxy component mixture (epoxy resin 1) to anhydride hardener

mixture (hardener 1 + maleinated soybean oil) of 100 : 80 is selected. Each of the mixtures is then filled with Somasif ADS (10 % by weight). The preparation of such nanocomposites is described by way of example below using the example of the moulding material modified with 50 % MASO.

In a tin container, 300 g of epoxy resin 1 and 60 g of Somasif ADS are stirred for 1 hour at 80°C/13 mbar using a planetary mixer, and then 120 g of hardener 1 and 120 g of MASO are added. The reaction mixture is pregelled at 80°C/13 mbar, with stirring, to give a viscosity of about 20 000 mPa.s and then, for the production of mouldings, is introduced into steel moulds of dimensions 200×200×4 mm and fully cured at 140°C for 14 hours.

The cast mouldings are milled to give test specimens and are subjected to the mechanical tests mentioned above. The mechanical properties so measured are listed in Table 2.

Table 2:

Example	7	8	9	10	11
epoxy resin 1 [g]	300	300	300	300	300
hardener 1 [g]	237.6	234	228	216	192
MASO [g]	2.4	6	12	24	48
Somasif ADS [g]	60	60	60	60	60
modulus of elasticity [MPa]	4404	4335	4296	4160	3903
tensile strength [N/mm ²]	74	75	68	67	64
K _{1C} [MPa·m ^{1/2}]	1.1	1.07	1.06	1.05	1.04
G _{1C} [J/m ²]	252	240	238	244	254

What is claimed is:

1. A composition comprising
 - (A) a resin mixture consisting of
 - (A1) from 0.5 to 50.0 % by weight, based on the sum of components A1 + A2, of an epoxidised or maleinated natural or synthetic oil, and
 - (A2) from 50.0 to 99.5 % by weight, based on the sum of components A1 + A2, of a polymerisable or curable monomer or monomer mixture other than A1, and
 - (B) an organophilic layer silicate obtainable by treatment of a natural or synthetic layer silicate with a swelling agent selected from sulfonium, phosphonium and ammonium compounds, but in the case where component A1 is an epoxidised oil, salts of melamine compounds and cyclic amidine compounds are excluded as ammonium compounds.
2. A composition according to claim 1, wherein component A1 is an epoxidised or maleinated oil based on mono- and poly-fatty acids having from 12 to 22 carbon atoms or an epoxidised or maleinated rubber.
3. A composition according to claim 1, wherein component A1 is an epoxidised or maleinated soybean oil or linseed oil.
4. A composition according to claim 1, wherein component A2 is a mixture of a polyisocyanate and a polyol or a mixture of an epoxy resin having more than one 1,2-epoxy group in the molecule and a hardener for the epoxy resin.
5. A composition according to claim 4, wherein component A2 is a mixture of an epoxy resin and a hardener, the epoxy resin being a fluid or viscous polyglycidyl ether or polyglycidyl ester or a mixture of such compounds.
6. A composition according to claim 5, wherein the epoxy resin is bisphenol A diglycidyl ether or bisphenol F diglycidyl ether.
7. A composition according to claim 5, wherein the hardener is an amine, a carboxylic acid, a carboxylic acid anhydride or a phenol.

8. A composition according to claim 4, wherein component A2 is a mixture of a polyisocyanate having at least two isocyanate groups and a polyol having at least two hydroxyl groups.
9. A composition according to claim 1, wherein for the preparation of the organophilic layer silicate B there is used bentonite, vermiculite, halloysite, saponite, beidellite, nontronite, hectorite, sauconite, stevensite or montmorillonite.
10. A composition according to claim 1, wherein for the preparation of the organophilic layer silicate B there is used a layer silicate of the formula $(\text{Al}_{3.15}\text{Mg}_{0.85})\text{Si}_{8.00}\text{O}_{20}(\text{OH})_4\text{X}_{11.8} \cdot n\text{H}_2\text{O}$, wherein X is an exchangeable cation and some of the hydroxyl groups may have been replaced by fluoride ions.
11. A composition according to claim 1, wherein for the preparation of the organophilic layer silicate B there is used a layer silicate having a layer spacing of from 0.7 nm to 1.2 nm and a cation exchange capacity in the range of from 50 to 200 meq./100 g.
12. A composition according to claim 1 containing from 0.5 to 30 % by weight of component B, based on the weight of component A.
13. A process for the preparation of a nanocomposite, wherein a composition according to claim 1 is solidified by curing or polymerisation of component A.
14. The use of the compositions according to the invention according to claim 1 in the production of paints/varnishes, adhesives, casting resins, coatings, fireproofing agents, thixotropic agents or reinforcing agents.

**UTILITY DECLARATION
AND POWER OF ATTORNEY
Utility Application**

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Nanocomposites

the specification of which

- ☐ is attached hereto OR
☐ was filed on ___ as United States Application Serial No. ___ OR
☒ was filed on 06/07/00 as PCT International Application No. PCT/EP 00/06422
☐ and was amended on ___ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment(s) referred to above.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, § 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or of any PCT international application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Date of Filing (day/month/year)	Priority Claimed	
			Yes	No
1288/99	Switzerland	13/07/99	<input checked="" type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>

I hereby claim the benefit under Title 35, United States Code § 119(e) of any United States provisional application(s) listed below.

Application Number(s)	Filing Date (day/month/year)

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s), or § 365(c) of any PCT international application designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT international application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

U.S. Parent Application Number	PCT Parent Number	Parent Filing Date (day/month/year)	Status-Patented, Pending or Abandoned

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POWER OF ATTORNEY: As a named inventor, I hereby appoint as my attorneys and/or agents, with full power of substitution and revocation, to prosecute this application and transact all business in the United States Patent and Trademark Office, and in countries other than the United States, and to do all things necessary or appropriate therefor before any competent International Authorities in connection with any international patent application(s) corresponding to the above-identified invention application, all of the registered practitioners identified by Customer Number 22249:



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I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Title 18, United States Code, § 1001 and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

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